
SUMMARY REPORT
STUDY TO DETERMINE THE
THERMOPHYSICAL PROPERTIES OF
ABLATIVE MATERIALS

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SUMMARY REPORT

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PROPERTIES OF ABLATIVE MATERIALS

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TABLE OF CONTENTS

| | Page |
|--|------|
| I. INTRODUCTION | 1 |
| II. STUDY OBJECTIVES | 1 |
| III. RELATIONSHIP TO OTHER NASA EFFORTS | 1 |
| IV. METHOD OF APPROACH AND PRINCIPAL ASSUMPTIONS. | 1 |
| V. BASIC DATA AND SIGNIFICANT RESULTS | 2 |
| A. Laboratory Measurements | 3 |
| A.1 Heat Capacity Measurements | 3 |
| A.2 Density Measurements | 4 |
| A.3 Thermal Conductivity Measurements. | 4 |
| A.4 Thermal Diffusivity Determination | 5 |
| A.5 Resin Decomposition Temperature | 6 |
| A.6 Char Melting and Decomposition Temperature Measurements | 6 |
| A.7 Emissivity Determination | 7 |
| B. Phase II, Ablative Engine Firings | 7 |
| VI. IMPLICATIONS FOR RESEARCH. | 8 |
| VII. SUGGESTED ADDITIONAL EFFORT. | 8 |

I. INTRODUCTION

This is the final summary report describing the work performed by TRW Systems under Contract NAS 9-4518, "Study to Determine the Thermophysical Properties of Ablative Materials." This contract was sponsored by the National Aeronautics and Space Administration under the technical direction of the Manned Spacecraft Center, Houston, Texas. The program, which represented a 17-month effort, was comprised of a comprehensive analytical, laboratory and experimental engine test program.

II. STUDY OBJECTIVES

The primary objective of the program was to determine the thermophysical properties of the following ablative materials:

- Fiberite MX 2600
- HITCO Irish Refrasil/Phenolic Resin
- Refrasil Cloth/Elastomeric Modified Phenolic Resin
- Fiberite MX 2646
- Magnesium Hydroxide/Phenolic Resin

III. RELATIONSHIP TO OTHER NASA EFFORTS

The data obtained under the contract has direct application to the primary propulsion engines on the LEM spacecraft, and service module. In addition, the thermophysical property data represents an addition to the basic property data that represent the state-of-the-art and technology of the materials investigated.

IV. METHOD OF APPROACH AND PRINCIPAL ASSUMPTIONS

The program was conducted in two phases. Phase I consisted of laboratory investigations to determine the thermophysical properties of the ablative materials under laboratory controlled conditions. The properties that were determined were:

- Specific heat (virgin and char)
- Density (virgin and char)
- Thermal conductivity (virgin and char)
- Thermal diffusivity (virgin and char)

- Resin decomposition (charring) temperature)
- Melting temperature (and char decomposition temperature)
- Surface emissivity (virgin and char)

The variation of these properties with temperature was also determined. Only the molecular transport properties were determined during Phase I. The decomposition kinetics of the resin system as well as the mass transfer of the decomposed gases through the char matrix was not investigated.

Under Phase II of the program, ablative liners instrumented with surface and in-wall thermocouples were tested. Two chambers were evaluated for each of the five materials studied. A total of 40 ablative thermocouples were installed in each chamber. These internal wall-response data were used to determine whether the data obtained under controlled laboratory conditions could be extrapolated to the dynamic engine environment to predict the measured temperature responses. It was also desirable to determine the "total thermal conductivity" of the charred material (i. e., the thermal conductivity that allows the prediction of the measured temperature response within the char layer).

Engine tests were conducted at a nominal sea-level thrust of 1000 lb_f, at a chamber pressure of 100 psia, utilizing the N₂O₄/UDMH-N₂H₄ (50-50) propellant combination at a nominal oxidizer-to-fuel mixture ratio of 1.6. This propellant combination, mixture ratio and chamber pressure, are the propellant combination and chamber conditions under which the Apollo engines are operated. Each material was tested under a combustion environment condition which was typical of its service environment.

V. BASIC DATA AND SIGNIFICANT RESULTS

Included in this section is a summary of the accomplishments of each phase of the "Study to Determine the Thermophysical Properties of Ablative Materials" program. In-depth discussions of each of the areas presented in this section may be found in the following sections of the final report.¹

¹ TRW Systems Report 04812-6002-R000, "Study to Determine the Thermophysical Properties of Ablative Materials" prepared under contract NAS 9-4518, dated 1 February 1967.

- Section 4.0: Phase I, Laboratory Measurements
- Section 5.0: Experimental Engine Firings
- Section 6.0: Data Analysis Procedures and Results

A. Laboratory Measurements

Under Phase I, laboratory measurements were performed to determine the following thermophysical properties, as a function of temperature for each of the five materials investigated:

- Heat capacity (both char and virgin)
- Density (both char and virgin)
- Decomposition temperature
- Melt temperature
- Thermal conductivity (both char and virgin)
- Thermal diffusivity (both char and virgin)
- Emissivity (both char and virgin)

These property variations were determined as a function of temperature up to 1800°F. Where possible, the data were extrapolated from 1800°F to 3000°F.

A.1 Heat Capacity Measurements

Heat capacity measurements were conducted as a function of temperature on both virgin and charred materials. Measurements on the virgin materials were made utilizing a Perkin-Elmer Model DSC-1 Differential Scan Calorimeter. The heat capacity of the charred materials was measured in the temperature range of 630°F to 1710°F with a modified Smith Calorimeter. There was good agreement between measurements made with the Differential Scan Calorimeter and the Smith Calorimeter. In general, the Smith Calorimeter data were slightly higher. An extrapolation of these data to 3000°F is provided.

None of the materials investigated exhibited a wide variation of specific heat with temperature. Each of the charred materials investigated had essentially the same specific heat. Of the virgin materials: the Fiberite MX 2600, Fiberite MX 2646 and the Western Backing Corporation 2234 (Irish Refrasil) had the same specific heat with values ranging from 0.22 to 0.28 Btu/lb-°F over the temperature range of 0° to 400°F. The U.S. Polymeric XR 2015 (silica/elastomeric modified phenolic) and the Western Backing Corporation 5217 (magnesium hydroxide/phenolic) had values of specific heat of 0.26 and 0.30 Btu/lb-°F at 0°F and 0.34 and 0.41 Btu/lb-°F at 400°F, respectively.

A.2 Density Measurements

Bulk density measurements in the temperature range of 77° to 1652°F were conducted with 3/4-inch cube samples of each of the five virgin and charred ablative materials. Densities were computed based on the weight of the sample after exposure for one hour and on the steady-state volume of the sample at the experimental temperature.

As with the heat capacity measurements, the basic silica phenolic materials (MX 2600, MX 2646, and the WBC 2234) exhibited the same dependence of density with temperature as well as approximately the same percent weight loss during charring. The virgin WBC 5217 material had approximately the same dependence with increasing temperature as the above materials. However, in the char state it exhibited 20 percent more weight loss than any of the materials. This additional weight loss includes a substantial contribution from the water evolved from the hydrated magnesium hydroxide fibers. The XR 2015 material, though lower in density than the above materials, showed about the same percentage change in weight as the basic silica-phenolic materials.

A.3 Thermal Conductivity Measurements

Thermal conductivity measurements were conducted as a function of temperature on both virgin and charred materials. Determinations covered a temperature range of 220° to 450°F for the virgin materials and a range of 420° to 1760°F for the charred specimens. Measurements were made using a specially designed twin-guarded hot-plate apparatus

which was maintained in a vacuum environment. Several unique design features of the apparatus permitted measurements of temperature up to 1800°F.

The virgin material measurements were, in general, somewhat higher than that reported in the literature. The polyamide modified MX 2646 had the lowest thermal conductivity with a mean value of 3 Btu-in/ft²-hr-°F. The XR 2015 material had a slightly higher value (3.5 Btu-in/ft²-hr-°F) of thermal conductivity than the MX 2646 material. Both the MX 2600 and the WBC 2234 material had thermal conductivity values of approximately 6 Btu-in/ft²-hr-°F. The WBC 5217 material was substantially higher than any of the other materials with a value of approximately 8 Btu-in/ft²-hr-°F. All virgin materials exhibited a slight increase in thermal conductivity with increasing temperature.

The char thermal conductivity data exhibited an increase with increasing temperature. Very high values of thermal conductivity were measured at approximately 800°F. The relative ranking of the magnitude of the char thermal conductivity was the same as with the virgin materials. No measurements were conducted on the charred WBC 5217 material because it did not maintain dimensional or structural integrity during charring.

All thermal conductivity measurements were conducted under vacuum conditions.

A.4 Thermal Diffusivity Determination

The thermal diffusivity of both virgin and charred ablative materials was calculated as a function of temperature using the measured thermal conductivity, heat capacity and density data.

Since the thermal diffusivity is a measure of the rate at which a material responds when subjected to heating, a meaningful ranking of materials in relation to their insulating ability can be obtained by ordering them as a function of increasing thermal diffusivity. The lower thermal diffusivity is characteristic of a better insulator. The relative ranking, in the order of increasing thermal diffusivity for both the virgin and char materials investigated, is presented below.

Table 1. Relative Ranking of Virgin and Charred Materials According to Increasing Thermal Diffusivity

| Material | Relative Ranking | |
|----------|------------------|-----------------|
| | Virgin | Char |
| MX 2646 | 1 | 1 |
| XR 2015 | 2 | 2 |
| WBC 5217 | 3 | No Measurements |
| MX 2600 | 4 | 4 |
| WBC 2234 | 5 | 3 |

A.5 Resin Decomposition Temperature

Thermogravimetric traces (TGA curves) were obtained using an Aminco Thermo-Grav to determine the resin decomposition temperature for all materials. The general shape of all the TGA curves were similar. It was determined that a specific decomposition temperature cannot be defined, but rather that decomposition occurs over a narrow temperature range. Rapid resin decomposition is observed to begin at about 600°F with complete resin decomposition occurring at about 1000°F. Each material decomposed over essentially the same temperature range. The temperature at the mid-point of the typical S shaped TGA curve, which is sometimes defined as the char temperature, was approximately 900°F for the MX 2600 and WBC 2234 material and was approximately 750°F for the remaining materials.

A.6 Char Melting and Decomposition Temperature Measurements

The temperature at which charred specimens of each of the five ablative materials either formed a liquid phase or rapidly decomposed was measured in a tungsten ribbon melting-point furnace. In addition, for the four materials which formed carbon-silica chars (MX 2600, MX 2646, WBC 2234 and XR 2015), measurements were made of the rate of carbon monoxide formation due to the reaction of carbon with silica.

The observed melting temperatures for all materials investigated fell in the temperature range of 3000° to 3300°F. These temperatures compare reasonably well with the maximum measured temperatures

obtained under engine firing conditions of approximately 3000°F.

Measurements also indicated that the formation of carbon monoxide from the reaction of the silica reinforcement (SiO_2) with the carbonaceous char residue proceeded very rapidly in the 2300° to 2500°F temperature region.

A.7 Emissivity Determination

The directional emittance of both the virgin and charred ablative materials was determined using a modified paraboloid reflectometer. Virgin property measurements were determined from the laboratory prepared specimens only. These measurements were limited to a maximum temperature of approximately 450°F due to the instability of the reflectance measurements caused by the first phases of resin decomposition. All of the virgin materials had emittance values in the range of 0.92 to 0.95. There was virtually no observed temperature dependence over the temperature range of 75°F to approximately 450°F.

The emittance was determined for both laboratory prepared char specimens and charred specimens taken from the tested ablative liners. All laboratory charred specimens had emittance values which fell in the range of 0.92 to 0.96. Measurements were conducted over the temperature range of 75° to 2250°F. There was little dependence of emittance on temperatures. Emittance data determined for the charred ablative liners was generally less than the emittance data obtained from the laboratory prepared charred specimens. Emittance values as low as 0.70 were determined for the WBC 2234 (Irish Refrasil) and XR 2015 material. An average value for the emittance was approximately 0.88. The emittance values for the MX 2600 material were the highest; the low temperature values were 0.96. The emittance appeared to drop off at the higher temperatures (above 1400°F) for all of the charred ablative materials taken from the engine. No measurements were conducted on the WBC 5217 material due to the lack of charred liner specimens.

B. Phase II, Ablative Engine Firings

Under Phase II of the program, fully-temperature-instrumented ablative chambers were tested to obtain ablative in-wall temperature responses for both the virgin and charred ablative liner. These measured temperature responses were then compared with those predicted

using the laboratory measured properties. Properties were then determined which predicted the measured temperature responses. These two sets of thermophysical properties were then compared, to determine whether properties determined under laboratory conditions could be applied to the dynamic engine environment to predict the measured transient temperature responses. Generally, the comparison of these two sets of thermophysical property data was not good. This conclusion applied to both the virgin and charred material thermophysical property data. Whereas all of the laboratory thermophysical property data indicated an increase in the basic properties (thermal diffusivity, α , and thermal conductivity, k) with increasing temperature, the properties determined from the measured temperature responses showed a very strong negative dependence of the basic properties with increasing temperature. In several cases, the comparison between properties was good.

As part of the injector checkout and trim test series, heat flux measurements were taken to characterize the wall thermal environment as a function of injector parameters. These measured heating rates were compared with empirical prediction techniques, and it was shown that the predicted heat transfer coefficients were as much as 50 percent lower than the measured values. These heat rejection data also provided the basis for the proper injector setting to assure a non-eroding ablative throat.

Comparisons made between maximum measured surface temperatures obtained from the ablative test firings, and those obtained from the laboratory measurements, showed good agreement.

VI. IMPLICATIONS FOR RESEARCH

No programs which can be classified as research are recommended.

VII. SUGGESTED ADDITIONAL EFFORT

It is recommended that additional technology programs be funded in the following areas:

- A. Laboratory studies should be conducted to determine the rates of decomposition of the resin system as well as the heat of decomposition of the resin system. The resultant gas products should be identified and their behavior in the charring ablator should be determined.

- B. Controlled laboratory experiments should be conducted to determine the reaction rates and activation energies of the char decomposition reactions.
- C. Additional emissivity experiments should also be performed to determine the transmissivity at high temperatures as well as the effects of heating environments (charring history) on emittance.
- D. A program should be initiated to establish experimental techniques and procedures for in-wall instrumentation capable of measuring accurate transient temperatures in insulating materials.
- E. Work should be performed to improve and establish techniques for the characterization of the combustion chamber wall thermo-chemical environment within rocket engines. Included should be a detailed evaluation of the existing empirical heat transfer prediction techniques.
- F. The work performed under this contract should be extended to new materials, particularly to those materials applicable to the new high energy earth storable and space storable propellant systems.